IMPERIAL BUREAU OF ENTOMOLOGICAL
24 AUG. 1939
INSTITUTE

THE

SCIENTIFIC PROCEEDINGS

OF THE

ROYAL DUBLIN SOCIETY

Vol. 22, N.S., Nos. 15–17. AUGUST, 1939.

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[*Authors alone are responsible for all opinions expressed in their Communications.*]

DUBLIN:

PUBLISHED BY THE ROYAL DUBLIN SOCIETY,

BALLSBRIDGE, DUBLIN.

HODGES, FIGGIS, AND CO.,

20 NASSAU STREET, DUBLIN.

WILLIAMS AND NORGATE,

36 GREAT RUSSELL STREET, LONDON, W.C. 1.

1939.

Price Two Shillings.

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No. 15.

LEAF MOVEMENT ON RELEASE OF SAP TENSION.

By HENRY H. DIXON, Sc.D., F.R.S.,
University Professor of Botany, Trinity College, Dublin,
AND
J. S. BARLEE, B.Sc.,
Assistant to the Professor of Botany, Trinity College, Dublin.

(Plate 4.)

[Read April 25. Published separately July 24, 1939.]

A little while after a transpiring branch is clamped very tightly in a screw vice the blades of its leaves tend to wilt and crumple, and its petioles to coil downwards. These curvatures may be in part attributed to the rising tension in the water columns connecting the distal parts of the leaves with the clamped end of the stem. In agreement with this explanation is the observation that when the clamped end of the stem is cut under water the crumpled blades and bent petioles straighten out, the supply of water below relieving the tension in the water columns in the tracheae (1).

It seemed desirable to repeat this experiment when atmospheric pressure was removed from the surface of the water-supply below, lest it might be thought that recovery of form of the transpiring organs was not conditioned by the relief of tension in the water but by the lifting force exerted by the weight of the atmosphere.

With this in view a small cylindrical glass vessel was arranged for the water supply (Fig. 1). This was fitted with a tightly fitting rubber bung furnished with three perforations—one to hold the connection with an air-pump (A), another to admit the lower end of the experimental branch (F), and the third, centrally placed, to allow the passage of a brass shaft (C), the rotation of which actuates a razor blade (E), which could cut off the lower end of the branch (F) submerged in the water contained in the cylinder. The hermetic closing round the shaft (C) was secured by a tapering shoulder on it ground into a similarly tapering sleeve of brass (B). The latter was fitted very tightly into the central hole of the bung. Into the second excentric perforation a tightly-fitting glass tube was introduced. This tube was provided with a slight constriction (D) as it passed through the bung, and on this a collar of rubber, fixed on the lower part of the branch, rested. This collar was conveniently made by slipping a piece of soft rubber tubing upon the branch

from its cut end. The arrangement of the collar is much facilitated by first slipping the tubing, lubricated with glycerine, on to the narrow end of a tapered glass tube, into which the end of the branch can fit. The rubber tubing may be now readily slipped from the tapered glass-tube on to the branch at the desired distance from the end. It should be so folded on itself that it is single below and double thickness above. This arrangement secures that it fits easily into the constricted glass tube fixed in the bung, and external pressure completes the seal. A somewhat similar seal to this has been described by Gregory (2).

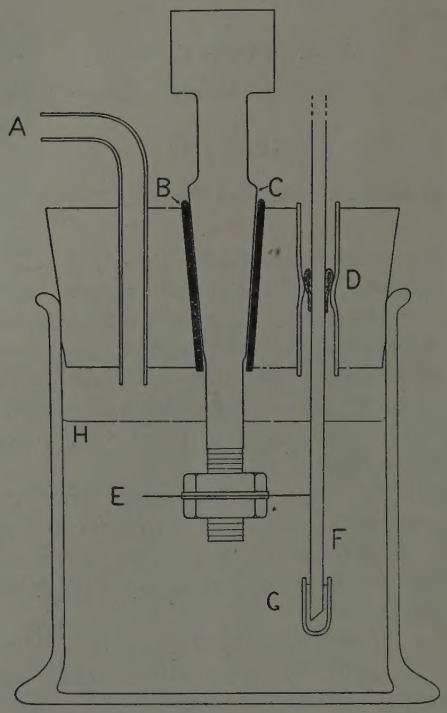

FIG. 1.—Vertical section of apparatus for cutting branches *in vacuo*, consisting of a cylindrical glass vessel closed with a large rubber bung. A, pipe leading to air-pump. B, brass coned sleeve fitted centrally in the bung. C, the coned shoulder on the shaft ground into B. D, gland for the experimental branch formed of a constricted glass tube supporting the rubber tubing slipped on to the branch F. E, Razor blade fixed on the lower end of the rotating shaft. F, lower part of the experimental branch carrying the gelatine glass shoe G.

Two methods were used for cutting off the water supply from the transpiring branch. (1) By clamping the lower end and crushing it tightly in a small screw clamp, which, when the branch was fixed in its tube, would be

submerged just below the cutting edge of the razor blade. (2) By fixing the lower extremity of the branch in a strong (25 per cent.) solution of gelatine contained in a thimble or shoe of glass (Fig. 1, G).

The method of procedure was then as follows:—The experimental branch selected as having a clear piece of stem (10–15 cm. long) below the side branch, or leaves, to be observed, was kept submerged in cooled boiled water for at least 24 hours. During this time the boiled water was changed 6–12 times. When injection was thus completed the rubber collar was arranged as described, and while still submerged in boiled water a new surface was cut on the branch-end, and it was introduced into the glass-shoe filled with liquefied gelatine (or crushed with the small screw clamp). When the gelatine was firmly set the razor blade was fixed on its brass shaft, and the bung, now carrying branch and cutting device, was pushed down into the top of the cylindrical vessel, which had been filled up to the level (H) with cooled boiled water. During

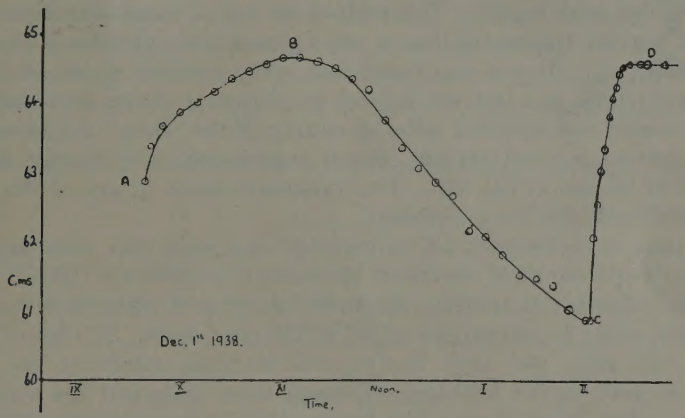

FIG. 2.—Graph showing the Vertical movement of the tip of the side-branch during the evaporation of surface water A–B, the rise of tension with transpiration B–C, and the release of tension C to D by the cutting off of the clamped submerged end in the vacuum cutter. Time is marked on the horizontal axis.

these operations transpiration was checked as far as possible by occasionally dipping the leafy parts of the branch in water, and by keeping them enveloped in a moist cloth. Connection was now made with the air-pump, and light capillary glass pointers fixed to the shoots or leaves under observation. The pump used was an electrically actuated Pfeiffer's air-pump, which readily reduced the vapour pressure in the "vacuum" cutter to 5 mm. Hg.

With these arrangements, save that the glass pointers were omitted, the following experiment was made, December 1, 1938 (results are plotted in Fig. 2):—A shoot of *Vitis striata* bearing an erect tapering and flexible side-branch about 20 cm. long was trimmed down to about 10 cm., and mounted,

as described, in the bung of the vacuum cutter. The side-branch carried 7 leaves. At zero time (11.40 a.m.) the pressure above the surface of the water was reduced to 0·5 cm. Hg. In 82 min. the tip of the side-branch had risen 1·6 cm. (probably due to gradual lightening of the branch by the evaporation of superficial water). Eight minutes later a downward bending (due to development of internal tension) became apparent, and this continued for approximately 3 hours. When the tip was 2·2 cm. lower than the starting point (A) and 3·8 cm. lower than B, the highest level reached before tension began to assert itself, the shoe was then cut off, and free access was given to the water below to relieve the tension in the branch. Immediately the tip rose rapidly (C–D), and in 24 min. attained the highest level from which it had been drawn down by the tension.

The graph reproduced in Fig. 2 summarizes the observations on which this record is based.

Experiments with the vacuum cutter were varied by the introduction of eosin into the water supply. This enabled the rise of water to be traced in the veins of various transpiring leaves when atmospheric pressure was removed from the supply. It was also found that, when a length of one of the main veins in the blade of a leaf was isolated by transverse section above and below before the eosin was admitted below by cutting off the "shoe," this intermediate portion became injected through lateral commissures very shortly after the injection of the rest of the vein. The translucent leaves of spp. of *Tropaeolum* are very suitable for this experiment.

In these experiments it not infrequently happened that stems and leaves continued to pursue their downward curvature even after the "shoe" was cut off. This behaviour is probably due to the starting of ruptures in the tensile columns of water by the cutting action of the razor blade. At these fractures bubbles will arise, and their menisci will hurriedly retreat to the nearest transverse walls in the tracheae. Between these walls and the evaporating surfaces in the leaves, tension will be immediately re-established, and cannot be relieved until pressure on the surface of the supply establishes continuity between the menisci in the tracheae and the water of the supply.

Fig. 3 (from a photograph taken with the ultropak microscope) shows ruptures developed in the water of the tracheae of a transpiring leaf on the application of local pressure. The results of several experiments carried out with the following modification of the former procedure are in complete harmony with this explanation.

In these experiments when it was observed that the downward curvature of the leaves or branch continued after the cutting off of the "shoe" atmospheric pressure was momentarily restored to the surface of the water-supply. Then the pump was again started, and the air pressure removed. In almost every case this initiated the straightening of the petioles and the branches. Fig. 4 shows a photographic record of one of these experiments. In it the leafy branch was placed in front of a black background, and to two leaves whitened

capillary pointers were fixed. Each exposure is registered by the minute-hand of the clock with the black dial. After each exposure a black mark was put on the white pointers. The first exposure was made while the "shoe" was still on, when the minute-hand is opposite 5 min., and before the pointers have received a mark. The "shoe" was cut off at 5½ min., and a mark was made on the end of each pointer. The second exposure was made at III. 08, and records the position of the pointers, each of which has now one black mark near its end. They were each a little lower than when the first exposure was made. Atmospheric pressure was applied at III. 08½, and it was maintained while the third exposure was made at III. 09½, and the position of the pointers, then carrying two marks, registered. At III. 09½ the vacuum was restored and a third mark added to each pointer, and the fourth exposure was made at III. 11. The successive exposures, made at III. 13, 15, 17, 19, 25, and 35, show the successive corresponding positions of the pointers distinguished there, respectively, with 4, 5, 6, 7, 8, and 9 marks. The rise, initiated by the healing of the rupture below the two leaves, has been continued throughout the 25 minutes. The last two exposures were four and nine minutes respectively after atmospheric pressure had been restored, and show that the final position assumed by the leaves, when *drawing* up the water columns—overcoming their weight and friction—was almost as high as that attained when atmospheric pressure was added below.

Table 1 gives the details of the experiments recorded in Fig. 4.

TABLE 1.

Exposure.	Hour.	Number of Dots on Pointers.	Pressure on Supply.
1	III.05 p.m.	0	Vacuum
	III.05½	"Shoe" cut off	,,
2	III.08	1	,,
	III.08½		Atm. press.
3	III.09	2	,,
	III.09½		Vacuum
4	III.11	3	,,
5	III.13	4	,,
6	III.15	5	,,
7	III.17	6	,,
8	III.19	7	,,
9	III.25	8	,,
10	III.35	9	,,
	III.36		Atm. press.
11	III.40	10	,,
12	III.45	11	,,

The details of a similar experiment (in which 4 leaves carried pointers) are presented in Table 2 and in Figs. 5 and 6:—

TABLE 2.

Exposure.	Hour.	Number of Dots on points.	Pressure on Supply.
1 Fig. 5	V.21 p.m.	0	Vacuum
	V.21½ "Shoe" off		,,
2 ,,	V.25	1	,,
	V.25½		Atm. press.
3 ,,	V.26	2	,,
4 ,,	V.27½	3	,,
	V.28		Vacuum
5 ,,	V.30	4	,,
6 ,,	V.35	5	,,
7 ,,	V.40	6	,,
Fig. 6	VII.41	6	Atm. press.

These and similar experiments seem to us to establish that the straightening of the bent petioles and branches is due to the release of tension in the contained water columns, and is not dependent on the action of atmospheric pressure forcing the columns upward in the water conduits.

They also clearly demonstrate that during transpiration the water in the tracheae supplying the leaves is in a state of tension.

We wish to thank Dr. L. A. P. Ballard for making the drawing from which Fig. 1 was prepared.

EXPLANATION OF PLATE 4.

Fig. 3.—Microphotograph taken with ultropak microscope, showing the appearance of a rupture started by local pressure of a needle point in a group of tracheae containing tensile water.

Fig. 4.—Photograph of the experimental arrangements showing the white capillary pointers and the method of correlating the positions of the pointers with the times indicated by the clock.

Fig. 5.—Similar photograph to Fig. 4, in which 4 leaves were equipped with pointers, and similar arrangements were made for correlating their positions with the times shown.

Fig. 6.—Final position of the leaves and their pointers used in the preceding experiment.

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2. GREGORY, F. G.—"A Convenient Method for Attaching Potometers." Ann. of Bot., Jan., 1938, p. 253.

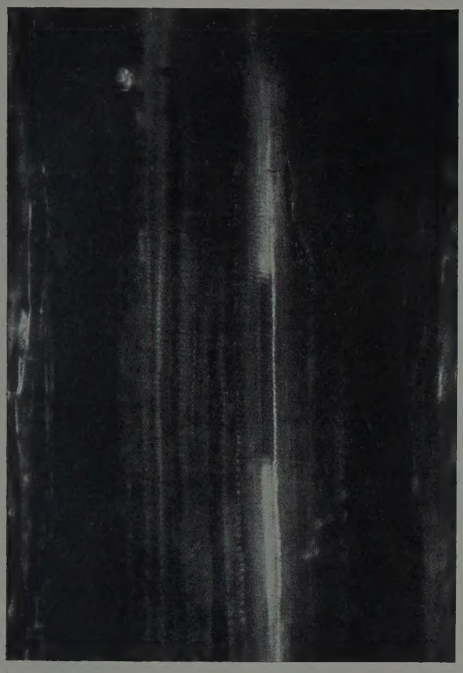

FIG. 3.

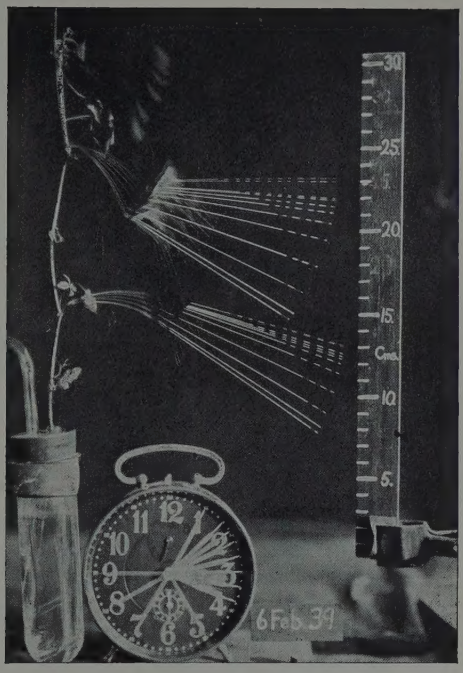

FIG. 4.

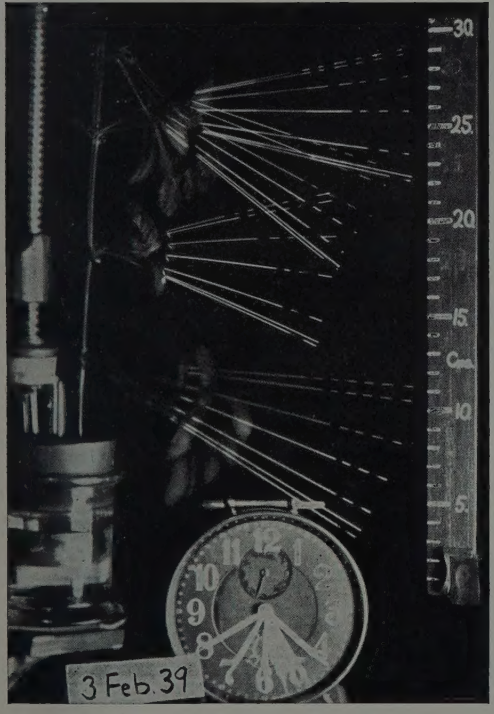

FIG. 5.

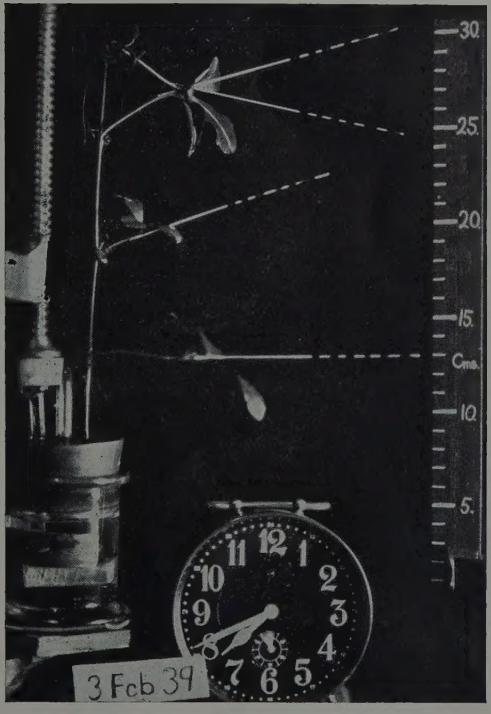

FIG. 6.

No. 16.

"STUDIES IN PEAT."

Part 6.

THE "WATER PHASE" IN AZEOTROPIC EXTRACTION SOLVENTS.

By J. REILLY and D. F. KELLY.

[Read June 20. Published separately July 24, 1939.]

Binary azeotropic and azeotrope-like mixtures of organic solvents have been found to possess advantages over single pure solvents in certain extraction processes (Reilly, Kelly, and Ryan, J. Soc. Chem. Ind., **56**, 231 T, 1937; Reilly *et al.*, Part 5, this series). When such mixtures are utilised in the extraction of peat the presence of moisture in the peat alters the conditions. The influence of such moisture on the mode of working the extraction process is considered in the present paper. It must be remembered that air-dried peat, such as would be employed for wax extraction purposes, contains as much as 30 per cent. of moisture.

The importance of ascertaining the behaviour of the water in the extraction process may best be indicated by examining the cycle of operations in a peat wax extraction plant. In this, the peat contained in a suitable vessel is submerged in the solvent, and digestion is allowed to take place at a suitable temperature. The solvent (containing the wax in solution) is next siphoned off on the lines of the usual soxhlet, or alternatively drawn off into a still (i.e., the "wax-still") with which the extraction plant is provided. It may be assumed that the water is for the greater part carried into the still at the end of this first digestion. From the still the solvent mixture is distilled off, and after condensation led into a storage vessel or tank with the water now in solution in the mixed solvent, from which it ordinarily is again led into contact with the peat, until the latter is exhausted of wax. The wax remains in the still to be run off eventually. As the same solvent mixture may be used to extract many succeeding batches of peat, in time it becomes necessary to remove water from the mixed solvents.

Where a single pure liquid immiscible with water (e.g., trichlorethylene) is used as a solvent the process of removing water becomes in most cases only that of mechanically removing the "water-phase." In extraction plants a "water-separator" is provided to run off in a continuous manner the water from the condensed solvent and water mixture before the solvent is returned to the storage tank. This arrangement also separates water from the mixture

(containing a large amount of water) obtained on the "steaming-out" of the last traces of solvent from the material under extraction. In peat extraction with azeotropic solvents, however, the water coming from the air-dried peat either mixes completely with the solvents or else forms a two-layer partially miscible system with them. The drying of peat to completion is generally not desirable, and the very dilute mixture of the azeotropic organic solvents in water obtained in the "steaming-out" process adds a further difficulty. The solvents containing a relatively low amount of water (say, 10 per cent.), such as would arise from one charge of air-dried peat in the extraction plant, do not inordinately interfere with the extraction process, independent of whether the mixture exists as a one- or two-liquid phase system (cf. Reilly *et al.*, *loc. cit.*, and Part 5, this series). Nevertheless, it is desirable to examine the difficulties attendant on the removal of water following the reaching of the point at which it begins to interfere with the extraction process.

The methods proposed for water removal will now be discussed. In the first instance attention will be directed to the behaviour on the simple distillation of the solvents from the "wax-still." This distillation is a necessary part of the process, but the incorporation of a fractionation here is felt not to be desirable. On the other hand, this necessary distillation carried out without fractionation with a column in the usual sense may be capable of playing a part in the dehydration of the solvents.

If the mixture of the wax solvents and water be distilled without fractionation, it has been found by us that the first portions of the distillate in many cases form two layers, one of which is rich in water, viz., the "water-phase." This is due to very volatile ternary (and possibly binary) azeotropes formed carrying most of the water with them in the early part of the distillation. On removing this water-rich layer the organic solvents could be recovered from it—for example, by fractionation, etc., a more concentrated mixture of the solvents may be obtained, and the water discarded. Alternatively, if dilute enough, as it would be in the ideal case, the whole layer or water-phase may be run to waste. The separated solvents may then be used over again, as they would have almost the original composition of the mixture. In the extraction plant the water-rich portions of the condensate obtained as above during the necessary distillation from the "wax-still" could be removed as the denser layer by, e.g., a continuous centrifuge or gravity separator.

At this point the methods available to meet the difficulties associated with removal of water from such solvent mixtures may be outlined briefly as follows:—(*a*) A method which has been applied in technical practice to benzene—ethyl alcohol solvent extraction mixtures (other than azeotropes) is that of adding a large volume of water to the mixture, thus causing complete separation of the benzene, followed by ordinary rectification of the alcohol from what is virtually a dilute mixture of alcohol and water. (*b*) A continuous process for the dehydration of ethyl alcohol is in technical use, i.e., the "Hiag" process, whereby a dehydrating agent of the nature of an inorganic salt is

dissolved in anhydrous alcohol; the solution is allowed to flow down a tower meeting an upward stream of "wet" alcohol vapour, from which the water is removed by interchange in the column, and "dried" alcohol vapour drawn off and recovered. We have found that certain dehydrating agents of similar nature to the above are soluble in the anhydrous azeotropic solvent mixtures employed in our work, so that it is possible to apply a novel variation of the method. The fact that inorganic dehydrating agents are soluble in anhydrous azeotropic mixtures is very striking, especially when it is remembered that many of them contain large amounts of aromatic liquids. It is hoped to describe fully elsewhere the full application of this method to the dehydration of azeotropic solvents. The method deals conveniently with the dilute "steaming-out" mixture to allow full solvent recovery in a convenient manner. (*c*) A continuous process where the wet solvent comes into contact with an insoluble solid dehydrating agent, e.g., calcium sulphate, such as in the case of the I.G. process for the dehydration of ethyl alcohol (rectified spirit) with continuous regeneration of the dehydrating agent. (*d*) The method of partial simple distillation as outlined in this paper, followed by removal of the "water-rich" layer (the first portions of distillate separating into layers), with or without dehydration of part only of the total solvent employed by one or other of the above methods. In general, the "water-rich" layer may be combined with the "steaming-out" distillate, and fractionation confined to this mixture.

For the application of the last-mentioned method a knowledge of the composition of the different layers of the ternary mixtures (i.e., "wet" azeotropic binary mixtures) when treated as above is of importance from the point of view of water removal (i.e., indirect drying of the peat) and solvent recovery in the possible extraction of waxes on the industrial scale using these mixtures of solvents. In the necessary experimental work to be described later (Part 7) the azeotropic mixtures selected for practical examination were those formed by benzene with each of the alcohols, ethyl, isopropyl, and n-propyl, and by certain petroleum fractions with the same alcohols. As the petroleum liquids consist of various hydrocarbons, the latter mixtures may best be described as "azeotrope-like" mixtures. It is assumed (as ascertained by us in a semi-large scale plant) for this work that 0·3 gallon of solvent is required in an extraction plant per 1 lb. of peat to be extracted, and that all the water in the peat passed into the solvent after the first digestion. In our experiments water is to be added to the solvent mixtures to correspond with peats of varying moisture content, and the mixture distilled until separation of the distillate into layers ceases. For this purpose the B.S.I. Distillation Apparatus No. 658 (1936) is used. Each layer (and, if necessary, the residual distilland) is then analysed, and the distribution of the water ascertained. The portion of solvent (i.e., conjugate solution) capable of being separated, by virtue of its having a different density from the other portion with which it is in contact, should have a high water-content for the full application of method (*d*) above.

Conditions obtaining in the distillation of solvent from wax in the still of an extraction plant (as described earlier) are duplicated (for all practical purposes) by this experimental method, since the presence of wax in solution does not interfere with the azeotropic nature or boiling point range of the mixtures (cf. Reilly *et al., loc. cit.,* and "Studies in Peat," Part 5). Although all of the wax is in solution in the solvent at the beginning of the distillation (as would occur after the first digestion in the "wax-still" of an extraction plant), a certain amount (proportional to the amount of solvent distilled) of the wax falls out of solution as distillation proceeds. Beyond a slight and constant raising of the boiling point, due to the relatively small amount of wax in actual solution, the azeotropic distillation behaviour is preserved. Incidentally (cf. also last-mentioned references) the presence of water does not again unduly interfere with the constancy of the boiling point of the mixtures. This is fortuitous, and probably due to the fact that the volatilities of the different components are not much different.

The manner in which the ternary mixtures behave on simple distillation will influence the choice of dehydration process to be employed. In general, the removal by distillation of the mixture of solvents and water from the still of the extraction plant may proceed in one of the following ways:—(1) The liquid mixture may exist in the still as a two-layer system, which for all of the distillation preserves this partially miscible character, the distillate also being found to exist as two liquid layers (one rich in water). (2) The liquid mixture in the still may exist first as a two-layer system, which, following the taking off of the more volatile components (containing most of the water), coalesces in the still at some point during the distillation. In this case it may occur that the denser layer of the distillate formed up to the point of coalescence would contain most of the water. Alternatively, in an unfavourable case the water may be found to be practically equally distributed between the two layers of the distillate and even the residual distilland. (3) The mixture in the still may exist as a single-phase liquid mixture. On distilling, the first portions of the distillate may again separate into two layers—one rich in water.

The particular category into which any solvent mixture may fall will depend on the amount of water present. If water be present in excessively large amount, all cases would fall into category (1) above, and the problem would become only that of alcohol distribution between, say, the petroleum fractions and water. This, of course, would not arise in a wax extraction plant, especially with mixtures of high "water tolerance," as undue increase in bulk of the solvent mixture following the addition of increasing amounts of water from successive batches of peat could not be accommodated in the plant, and further, the wax dissolution powers of the solvent mixture would be excessively diminished. In addition, the waste involved in continually distilling large amounts of water from the "wax-still" of the plant would not be entertained. On the other hand, the mixtures at the azeotropic composition possess different "water tolerances" (cf. Reilly *et al.,* J. Soc. Chem. Ind., *loc. cit.*), and we have

found that it is not possible to predict without experiment the behaviour on simple distillation. For example, one of the two-phase liquid mixtures may not persist as such during the whole of the distillation (cf. analogous heteroazeotropic mixtures—Swietolawski, "Ebulliometry," New York, 1936). It also requires experimental determination to ascertain if separation occurs in the first portions of the distillate from an originally coalesced distilland. It is necessary in addition to determine experimentally the water distribution in the different cases where separation of the distillate into two layers ceases before the end of the distillation. As azeotropic or azeotrope-like mixtures do not appear to have been employed heretofore in this connection, it is of interest to examine the behaviour of water from the above points of view when these solvents are used in the extraction of air-dried or other moisture-containing peat.

To sum up, an efficient solvent mixture, from the point of view of ease in solvent recovery, would be one which would give a relatively small amount of lower layer separation, with coalescence of the distilland if necessary, at an early stage in the simple distillation. The lower layer should contain most of the water added. In practice we have found that none of the mixtures examined agree completely with this ideal case. Yet many of the mixtures give sufficient approach to it, and so are of practical utility. The experimental behaviour of the mixtures in relation to the formation of a "water-phase" and their dehydration when used as solvents will be described in a later paper (Part 7).

Summary.

Water coming from moisture-containing substances (e.g., air-dried peat containing 30 per cent. moisture) entrains with the azeotropic solvents into the still of the plant used for extraction purposes. The water-containing azeotropic solvents (e.g., benzene and ethyl alcohol), or arbitrary azeotrope-like solvent mixtures (composed of certain petroleum fractions with the alcohols ethyl, iso-propyl, and n-propyl), may exist, after distilling part only of them from the still of a peat wax extraction plant, as two liquid-phase systems. The denser layer is rich in water—the "water-phase." The relation of this to other general methods for the dehydration of the mixed solvents is discussed in some detail.

The authors desire to thank the Industrial Research Council for permission to publish this paper.

No. 17.

"STUDIES IN PEAT."

PART 7.

WATER DISTRIBUTION IN PEAT WAX AZEOTROPIC EXTRACTION SOLVENTS.

BY J. REILLY, D. F. KELLY, J. DUFFY, AND E. COUGHLAN.

[Read JUNE 20. Published separately JULY 24, 1939.]

IN Part 6 of this series some methods were discussed whereby the removal of water entraining in azeotropic or azeotrope-like organic solvents could be conveniently effected in peat wax extraction processes. It was pointed out that distillation of the solvents from the "wax-still" of an extraction plant was a necessary part of the solvent extraction process. In some cases the first portions of distillate, obtained by this simple distillation of the water-containing solvents, separate into two layers. The lower layer of distillate is rich in water, and may virtually constitute a water-phase; mechanical separation of the latter removing water from the system. The exact compositions of the different portions of solvent (upper and lower layers of distillate and residual distilland) are of importance in ascertaining the feasibility of applying in practice this—or some other—method of water removal. These compositions have now been ascertained for azeotropic and azeotrope-like mixtures of benzene and certain petroleum fractions with the alcohols, ethyl, isopropyl, and n-propyl. The results are described in this paper.

In the experiments water was added to 30 c.c. of the azeotropic solvent mixtures in amounts to correspond with peats of moisture-content varying from 30 to 5 per cent. The mixtures were then distilled as described in Part 6. The amount of solvent mixtures taken in the experiments was 30 c.c., as this was a convenient amount (especially, as explained in Part 6, since 1 lb. peat $\equiv 0{\cdot}3$ gallon solvent). The total volume of the mixtures preparatory to distillation may be taken to be that of the sum of the volumes of the mixed solvent—30 c.c.—and of the water actually united, as volume changes on mixing were found to be negligible. For the pure aromatic solvent the azeotropic mixtures were made up with 5 per cent. by weight of the component of higher boiling point in excess of exact azeotropic composition. This was expected to offset in practice any deviation in azeotropic distillation behaviour due to the presence of wax in solution. The latter may be said to correspond to the effect of increased pressure on azeotropic composition. It was taken here as altering

the composition of the azeotrope, so that more of the higher boiling component entered the azeotropic composition.

In the case of the petroleum fractions, the compositions employed were those used by Reilly *et al.* (Part 5 of this series). The results obtained in the case of the pure aromatic hydrocarbon are summarised in Table 1. The figures under the reference letter S1 refer to the system benzene—ethyl alcohol, S2 to the system benzene—isopropyl alcohol, and S3 to that of benzene—n-propyl alcohol mixtures (as used for wax solvents in the presence of varying amounts of water).

TABLE I.

A.		B.			C.			D.			E.			F.		
(*a*)	(*b*)	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3	S1	S2	S3
3	30	2	2	2	26	33	33	4·9	3·2	3·7	38·3	41·2	71·6	40	—	—
2·5	25	2	2	2	24	35	32·5	4·7	3	2·8	34·8	40·2	64·4	45	—	—
2	20	1	2	2	23	32	32	3·25	1·9	2·3	34·7	42	42·3	42	—	—
1·5	15	1	2	2	18·25	25	22	2·5	1·25	1·35	14·5	30·4	19·0	56	23	30
1	10	1	2	2	8	16	15	0·9	0·66	0·93	4·3	14·6	12·6	69	44	49

A.—Number of c.c. of water added to 30 c.c. of solvent mixture (*a*); and corresponding % peat moisture content (*b*).

B.—Number of phases formed by resulting mixture.

C.—Total volume in c.c. of distillate collected when distillation carried out until separation of distillate into two layers ceases.

D.—Volume of lower layer of distillate in c.c.

E.—Lower layer of distillate contains % of total water added.

F.—Residual distilland contains % total water added.

It will be observed that in system S1, though the lower layer separation is in each case small, the percentage of total water in it is also small; also, the residual distilland contains an appreciably high percentage of the total water added, thus entailing treatment of both these portions of solvent for removal of water from the solvent mixture. In this case the water is fairly evenly distributed, and removal of water, if this mixture be employed, would appear to be best effected by methods (*a*) or (*b*) described in Part 6.

In the case of the benzene—isopropyl alcohol solvent (S2) it will be noticed from Table 1 that in the first three cases separation occurs throughout the distillation (water-tolerance of mixtures low), i.e., the separation is the same as in the distilland, and water distribution here becomes for all practical purposes that of isopropyl alcohol distribution between benzene and water. The lower layers are small, but here again the percentage of water in them is too low, since even by removal of it there is still left too high a proportion of water in the upper layers (there is no residual distilland in these cases except

for mixtures of low water-content) so that fractionation, etc., would have to be resorted to here also, and dehydration of the solvent mixture would best be effected by, e.g., methods (*a*) or (*b*) (cf. Part 6).

In the case of the first three mixtures in system S3 separation also occurs throughout the distillation. The lower layer separation is small, and in the first two mixtures this layer contains 71·6 and 64·4 per cent. of the total water added, which is an appreciable amount. The amount of water in the water-rich layer increases rapidly with the increase of total water, so that it would be possible to perform several extractions with a peat of 10 per cent. moisture-content, and remove the collected "water" layer at definite intervals when the water-content of the solvent mixture reaches, say, approximately 10 per cent.; again e.g., with a peat of 30 per cent. moisture-content the main bulk of the water could be removed by treating the (relatively small) lower layer by, e.g., methods (*b*) or (*c*) after each extraction. The absolute dehydration of the solvent mixtures is, of course, not necessary after the extractions, but merely the removal of enough water to prevent any deleterious effect on the dissolution power of the solvents, and to avoid the distillation of large amounts of water from the "wax-still." This solvent mixture is, therefore, the most efficient of the three (containing benzene) studied from the point of view of utilising the separation occurring during the necessary distillation of the azeotropic solvents from the "wax-still" to remove the water from the mixture.

The benzene systems were examined not only to investigate their possible behaviour in use as solvents for peat wax extraction, but to compare their properties with those of the arbitrary azeotrope-like petroleum mixtures. The petroleum mixtures give solvent combinations of economic cost which extract large yields of waxes from peat (cf. Part 5). The latter mixtures gave in some instances (viz., petroleum spirit Y2) striking results from the point of view of the possibility of applying fractionation to a part only of the total amount of solvent for the purpose of solvent recovery with, of course, simultaneous removal of water. The water-content of the lower layers in these cases is unexpectedly low, but the possibility of using wet peat with these mixtures, and removing the water entraining in the solvent by what may be termed an "inverse" modification of the short (*d*) method (cf. Part 6), is of considerable interest here.

The mixtures which were dealt with experimentally were: (1) Petroleum spirit Y2—ethyl alcohol (50 : 50 by volume); (2) Petroleum spirit Y3—ethyl alcohol (40 : 60) and Petroleum spirit Y3—n-propyl alcohol (50 : 50). The natures of the two petroleum spirits Y2 and Y3 were defined in Part 5 of this series. Table 2 gives the results obtained in the analysis of the first mixture above. This shows clearly the striking feature of distilling these petroleum-alcohol-water mixtures—viz., the amount of petroleum which separates out in the upper distillate layer even when the percentage of water in the original mixture is quite low. Thus, the simple distillation of the mixtures (as from the "wax-still" above) results in the separation of the bulk of the petroleum.

The residual distilland contains a high proportion of the total water added, and, since this now must largely consist of ethyl alcohol and water, the removal of the water (the residual distilland being obtained as a separate portion of solvent on continuing the distillation after separation of the distillate has ceased) may be for all practical purposes carried out by any of the standard methods for the simple rectification of aqueous alcohol. The lower layer may, of course, be added to the condensed distilland preparatory to the rectification. This obviates the dilution process, and its observation should be of interest. Similar results were obtained for the petroleum Y3—ethyl alcohol mixture examined. These mixtures are distinctly in contrast with the benzene (cf. Tables 1 and 2). An exception, however, occurs in the case of the petroleum spirit Y3—n-propyl alcohol mixture; the results obtained are similar to those

TABLE 2.

Y2 Spirit-Ethyl Alcohol (50 : 50 *by Volume*).

A.			B.			C.	D.	E.	F.	G.	H.
(*a*)	(*b*)	(*c*)	(*p*)	(*a*)	(*w*)						
3·5	35	2	41·92	44·26	13·82	22·5	8·5	27·6	65·6	95·5	88·2
2·5	25	2	43·61	46·41	9·98	22	8	36	56·8	96·2	88·1
1·5	15	2	45·41	48·36	6·23	22	8	26	56	94·7	86·7
0·5	5	1	47·37	50·51	2·12	15·5	7·5	25	67	81·9	41·2

A.—Number of c.c. of water added to 30 c.c. of solvent mixture (*a*), corresponding moisture-content of peat (*b*), and number of phases formed (*c*).

B.—% composition of resulting mixture by weight.
(*p*) = petrol; (*a*) = alcohol; (*w*) = water.

C.—Total volume in c.c. of distillate when distillation carried out until separation into two layers of distillate ceases.

D.—Volume of lower layer of distillate in c.c.

E.—% by weight in lower layer of distillate of total water added.

F.—% by weight in residual distilland of total water added.

G.—% by weight of petroleum in upper layer of distillate.

H.—% by weight of total petroleum in upper layer of distillate.

of benzene—n-propyl alcohol, as may be seen from Table 3. The lower layer separation is small, and consists largely of water; thus the conclusions arrived at in the case of benzene—n-propyl alcohol mixture apply here also. The important modification exists here, however, namely—that coalescence of the distilland occurs, though not at an early stage of the distillation. Nevertheless this is amply compensated for by the high water-content in the relatively small volume of lower layer, allowing method (*d*) to be applied in its entirety for dehydration purposes here. It is interesting to note that for the case of 5·9 per cent. water-content in the solvent, although the resultant mixture is a

one liquid-phase system, separation occurs for quite a large amount of the distillate from this. The water-content of the lower layer is also quite large. An analogous behaviour is immediately disclosed also in Table 2. With even

Table 3.

Y3 Spirit-n-Propyl Alcohol (50 : 50 *by Volume*).

A.			B			C.	D.	E.	F.
(*a*)	(*b*)	(*c*)	(*p*)	(*a*)	(*w*)				
3·5	35	2	43·6	43·7	12·7	25	3	91	76
2·5	25	2	45·2	45·4	9·4	21	2	93	71
2	20	2	46·1	46·3	7·6	18	1·8	82·9	70
1·5	15	1	46·9	47·2	5·9	15	0·9	89·8	52

A.—Number of c.c. of water added to 30 c.c. of solvent mixture (*a*), corresponding moisture-content of peat (*b*), and number of phases formed (*c*).

B.—% composition of resulting mixture by weight.
(*p*) = petrol ; (*a*) = alcohol ; (*w*) = water.

C.—Total volume in c.c. of distillate when distillation carried out until separation into two layers of distillate.

D:—Volume of lower layer of distillate in c.c.

E.—% by weight of water in lower layer of distillate.

F.—% by weight in lower layer of distillate of total water added.

the one-phase mixture a very appreciable amount of the upper layer of the distillate consists of petroleum. For the remaining of the mixtures in Table 2 coalescence of the two-layer distilland occurs at approximately the same point, and the amount of petroleum in the upper layer would seem to be the maximum possible. Altogether, the petroleum-alcohol mixtures have proved to be of considerable interest, not only from the point of view of yield of wax (cf. Part 5), but also, as is now shown, of ease in water removal from their mixtures with the alcohols.

Preparation of Solvents.

Previously dehydrated hydrocarbons and alcohols were used in making up the mixture of solvents used in the investigation; distilled water being then added to the pure solvents to make up the particular "wet" mixture required. For dehydrating the solvents employed different methods were adopted. The hydrocarbons were shaken up with calcium chloride, while the alcohols were dehydrated as follows:—They were distilled twice from anhydrous copper sulphate, using a Young fractionating column, and were then treated with aluminium amalgam (cf. Neissberger and Proskamer, "Organic Solvents," London, 1935). To make the latter, aluminium chippings were degreased,

treated with alkali until there was a vigorous evolution of hydrogen, and then washed with a little water until the washing was weakly alkaline. They were next dipped for a few seconds in a 1 per cent. solution of mercuric chloride. After two minutes the chippings were washed with water, with alcohol, and then with ether, and finally dried with filter paper. The amalgam was added to the alcohol (first treated as above), and this gently warmed till the evolution of hydrogen ceased. The alcohol was afterwards re-distilled, using a Young column. This method gave alcohols of less than 0·2 per cent. water-content, and the water-content of the amount of alcohols used in making up 30 c.cs. of the solvent-mixtures was consequently neglected.

Analysis of Layers.

The compositions of the upper distillate layer and of the residual distilland were directly determined, and the composition of the lower distillate layer found by difference. Actually, the amounts of water and alcohol present in each mixture for analysis were determined; the hydrocarbons being calculated by subtraction. It may be mentioned that a method of estimating the hydrocarbon body, e.g., benzene, sometimes used in solvent analysis was found too inaccurate for the present purpose. This method involves the distillation of a sample of mixture with at least ten times its weight of water till the thermometer indicates 95 degrees C., when all the hydrocarbon should have passed over. The distillate is then washed with an equal volume of water when it may be considered that the volume of the upper layer represents the totality of the hydrocarbon in the sample taken. In control experiments it was found, however, that there was an error of 10 per cent. approx. in each estimation in the cases met with in this work, and consequently it was decided to determine the concentration of the alcohols directly. Barbaudy's (Bull. Soc. Chem., **40**, 695, 1926) physical method for analysis of alcohol—benzene—water mixtures is very accurate. Here the density and refractive index of a mixture gives at once the composition. However, as it is applied only to the system of ethyl alcohol—benzene—water, a chemical analysis was effected for the estimation of both the alcohols and the water in all of the present cases.

Estimation of Water Content of Layers.

The water present in the layers was estimated by the method of Dietrich and Conrad (Z. Angew. Chem., **44**, 532–4, 1931) by using magnesium nitride. The water reacts with the magnesium nitride according to the equation $Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3$, and the ammonia evolved is estimated by trapping in standard acid. Magnesium nitride (Kahlbaum, made especially for water determination) was used in this work; that used by Dietrich and Conrad was prepared by them by passing dried nitrogen through a glass tube containing magnesium powder and heating to incandescence. In the estimation

the magnesium nitride is put in a dried flask (A), and covered with anhydrous petrol (dried over calcium chloride). The quantity of magnesium nitride used is about double the amount calculated as approximately necessary for the water-content, but it is recommended that in no case must it be less than 5 g. The flask is well closed by a two-holed rubber stopper. A dropping funnel (B) passes through one, and a distillate outlet tube (C) through the other hole of the stopper. A double surface condenser is attached to (C), which communicates with a flask (D) containing standard sulphuric acid. The portion of layer to be analysed (abstracted from the layer by a Lunge pipette) is placed in (B), and is allowed to flow slowly from the funnel into (A), which contains the magnesium nitride and petrol. The funnel (B) is then washed down—first with anhydrous alcohol, and afterwards with anhydrous petrol. The ammonia evolved on the interaction of the water and magnesium nitride passes along (C) to (D), and is fixed quantitatively by the standard sulphuric acid. The flask (A) is heated slowly on a wire gauze until about three-quarters of its contents have passed over. In later determinations an all-glass apparatus, made to our design by Messrs. Quickfit and Quartz, Ltd., was employed, and found much more convenient for the routine work involved in the estimation of the water-content of the large numbers of mixtures made up for this work.

Determination of the Alcohols.

Ethyl alcohol was estimated by the oxidation method recommended by Adams and Nicholls (Analyst, **54**, 29, 1929). As used in this work, a sample of layer containing not more than 1·5 g. of ethyl alcohol was diluted to 100 c.c. with water, and an oxidising mixture of 10 g. potassium dichromate and 25 c.c. of concentrated sulphuric acid diluted to 100 c.c. with water added. After half-an-hour excess of ferrous sulphate is added, and the mixture steam distilled, the contents being allowed to concentrate to 100 c.c. The whole of the acetic acid formed has passed over when the distillate reaches a bulk of 500–600 c.c. The acetic acid is then titrated with N.NaOH solution, solid phenolphthalein being added as indicator. The addition of common salt makes the end-point sharper. (1 c.c. of N.NaOH = 0·046 g. of ethyl alcohol.)

N-propyl alcohol was estimated likewise. This gives under similar oxidation conditions a mixture of propionic and acetic acids, and here 1 c.c. N.NaOH = 0·060 g. of n-propyl alcohol.

The isopropyl alcohol presents a little more difficulty in its estimation. Here acetone is formed in the oxidation process, and this was determined by Messinger's method.

Summary.

The paper records the experimental results for the water-distribution obtained by partial simple distillation of "wet" azeotropic or azeotrope-like

solvents, as used in the extraction of wax from moisture-containing peat. The water is distributed between the upper and lower layers of the distillate and the residual distilland. Water-rich lower layers allow of ease in removal of water from the extraction system. In the case of certain azeotrope-like mixtures of petroleum spirits with ethyl alcohol, the upper layer is very rich in the total petroleum present, although complete distillation was not necessary. The dehydration of such mixtures is virtually that of the rectification of aqueous alcohol. The general methods by which the solvents may be dehydrated are also indicated.

The authors wish to thank the Industrial Research Council for facilities to carry out this work and for permission to publish.

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